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AGC 1030-82Q-8

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON
BINDER FOR HIGH ENERGY SOLID PROPELLANTS

by

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Chemical & Physical Sciences Section
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Sacramento, California

Quarterly Technical Report AFRPL-TR-68-64

April 1968

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Air Force Rocket Propulsion Laboratory
Research and Technology Operations
Edwards, California 93523
Air Force Systems Command, United States Air Force

AFRPL-TR-68-64

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FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11419 as partial fulfillment of the requirements of Project 3418 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work reported was done in the Chemical and Physical Sciences Section of the Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Corporation Report 1030-82Q-8 and covers the results of work done during the interval 14 December 1967 to 13 March 1968. The project was a follow-on to the project completed under Contract AF 04(611)-10386, the results of which are reported in Report No. AFRPL-TR-66-40. Phases One to Three of this program have been completed and the results (including Phase Four results) are reported in AFRPL-TR-67-158. This document reports on Phases Four and Five. This project was monitored by Mr. Robert Corley.

Acknowledgment is made to the following persons who have contributed materially to the work performed during this period: A. J. Hammond, Senior Chemist, J. L. Humphreys and T. F. Manning, Chemists, F. H. Davidson, Liaison Engineer, Mechanical Properties Laboratories; and at The General Tire and Rubber Company to R. G. Chase, Technical Assistant to the Technical Coordinator, Research and Development.

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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

The study of saturated prepolymers as propellant binder ingredients was centered predominantly on partially (50-60%) saturated prepolymers. The partially saturated propellants showed a threefold improvement of properties at -75°F . The type of crosslinker, CTI, GTRO, or LHT-240, did not affect the properties in a major fashion. The study of the LHT-240 which improved the low temperature properties of partially saturated propellants made on an IRAD program is continuing. Because more emphasis was being placed on partially saturated prepolymers, the oxidative surface hardening of binders made with saturated, partially saturated, and unsaturated prepolymers was investigated. The saturated binders showed no surface hardening after eight weeks at 80°C . Initially, the partially saturated binder hardened more rapidly than the unsaturated one, but the difference decreased with time. After eight weeks the unsaturated binder was hardening more rapidly. Propellant stability was greatly improved by a copper (II) additive and the feasibility of isocyanate-cured propellants for very high temperature use was demonstrated.

The use of blocked isocyanates as cure agents for propellants with advanced oxidizers was studied in model systems. Carbamates which dissociate at 60°C to produce isocyanate were tested in the presence of oxidizers. Tin catalysts help and oxidizers inhibit the cure reaction. Carbamates with dissociation temperatures of 30° to 40°C are desirable.

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GLOSSARY

Antioxidant 2246	2,2'-Dihydroxy-4,4'-dimethyl-6,6'-di- <i>t</i> -butyl-diphenylmethane
C ₁ and C ₂	Mooney-Rivlin Constants
C-1	N,N-di-(2-cyanoethyl)-2,3-dihydroxypropylamine
Carwinate M-125	4,4'-Diisocyanatodiphenylmethane, product of the Upjohn Company
CTI	Triisocyanate, proprietary item of the Aerojet-General Corporation
DEA	Diethanolamine
DEHT	Peroxide scavenger
E ₀	Initial uniaxial modulus
E-246	Multifunctional isocyanate, product of Mobay Chemical Company
FeAA	Ferric acetylacetonate
GLC	Gas-liquid chromatography
GTRO	Glycerol triricinoleate
HAA	Acetylacetone
HDI	Hexamethylene diisocyanate
IDP	Isodecyl pelargonate, product of Emery Industries, Inc.
LHT-240	Polyether triol, product of Union Carbide Company
P-33	Carbon black
PAPI	Polyphenyl polyisocyanate, product of the OPR Division, Upjohn Company
PBNA	Phenyl-β-naphthylamine
T-20	Organo-sulfur tin compound

GLOSSARY (Cont.)

TBTO	Bis-(tri-n-butyltin)oxide
Telagen	Functionally-terminated polybutadiene, product of The General Tire and Rubber Company
Telagen S	Functionally-terminated hydrogenated polybutadiene, product of The General Tire and Rubber Company
TEPAN	Oxidizer bonding agent
TDI	Toluene diisocyanate
VPO	Vapor phase osmometer
ϵ_b	Uniaxial strain at break
ϵ_r	Maximum uniaxial strain
σ_b	Uniaxial break stress
σ_u	Uniaxial maximum stress

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER
FOR HIGH ENERGY SOLID PROPELLANTS

I. INTRODUCTION

This is the eighth Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11419. The report covers the period 14 December 1967 through 13 March 1968.

II. OBJECTIVE

The objective of this program is to further develop and evaluate a solid propellant binder system specifically to meet the most rigid demands of advanced high performance solid rocket motors. The solid propellant binder system consists of an isocyanate-cured, hydrocarbon prepolymer developed and evaluated under Contract AF 04(611)-10386. Further development and evaluation will involve use of partially saturated prepolymers, propellant optimization, testing of curatives for room temperature cures, replacing CTI, attaining better low temperature properties, determining the effect of burning rate modifiers, adaptation to an advanced oxidizer, and a study of environmental stability.

III. SUMMARY

A. The antioxidant content of prepolymers used for binder stability studies was determined. The related Prepolymers 242AM-169, 3HPL-123, and 3HPL-125 had 0.1% antioxidant, while the related Prepolymers 242AM-175B and 3HPL-90 had 0.06 and 0.04%, respectively.

B. Mobay E-246 was separated into solid and liquid phases by cooling. While each phase had the same equivalent weight, the solid phase was higher in molecular weight and functionality.

C. PAPI was also fractionated by a 90 to 10 ratio of hexane and toluene. The soluble fraction was straw-colored and its infrared spectrum was similar to that of E-246.

D. A propellant prepared with a difunctional prepolymer obtained by chromatographing Prepolymer 158H had the properties, $\sigma_c = 231$ psi, $e_c = 7.4\%$, and $E = 3620$ psi, at 77°F and $\sigma_c = 966$ psi, $e_c = 3.6\%$, and $E = 37300$ psi at -75°F . A valid comparison with propellants made with Prepolymer 158H was not possible because of the very high modulus of the propellant made with the difunctional prepolymer.

E. The unsaturated prepolymer, Lot 242AM-148A, the precursor of the saturated prepolymer, 242AM-148AH, studied extensively at Aerojet and at Esso, was chromatographed on silica gel. The unsaturated prepolymer contained 30%

monofunctional material and no appreciable nonfunctional material. This indicates that the monofunctional prepolymer originates during the manufacture of the unsaturated prepolymer and that nonfunctional material is formed during the hydrogenation process.

F. Room temperature cures were obtained with Telagen S binder with CTI and GTHO as crosslinkers. Mobay E-246 is a candidate crosslinker for replacement of CTI. Propellant crosslinked with Mobay's E-246 and containing a curing system which ensures long potlife gave good mechanical properties at 77° and -75°F. The cure system using curative developed on an IR&D program to increase potlife has been demonstrated to be effective with the hydrocarbon prepolymers used on this program.

G. No improvement in mechanical properties was obtained when the bonding agent C-1 was replaced by TEPAN in a propellant containing a partially hydrogenated prepolymer. Increasing the amount of C-1 from 0.1 to 0.3 wt% improved the low temperature properties of partially saturated hydrocarbon propellant.

H. Propellant properties of the last three prepolymers received from The General Tire and Rubber Company continue to substantiate the fact that the low temperature properties are a function of the degree of unsaturation of the prepolymer. The polyether triol, LHT-240, was used in place of CTI in saturated, and partially saturated hydrocarbon propellants, but no improvement in low temperature properties was observed. Further propellant changes are being introduced to approach propellants similar to those prepared in an IR&D program and which showed very good low temperature properties.

I. Studies of effect of saturation on oxidative stability were continued into the eighth week. The surface hardening of partially saturated and unsaturated binders was becoming more nearly alike. Although initially the partially saturated ones hardened more rapidly, the unsaturated binders now show a more rapid rate of surface hardening. Further studies have been initiated, and propellant studies are in progress.

J. Stabilized propellants were aged for 2 weeks at 180°F and 50% relative humidity. A copper additive was a promising stabilizer. Hydrocarbon, isocyanate-cured propellants were exposed to 350°F for 2 hours. The main effect was hardening. Propellants containing a copper additive fared best in this test. These results are considered significant since they indicate the feasibility of isocyanate-cured propellants for high temperature use.

K. The blocked isocyanate, p-chlorophenyl N-phenylcarbamate, was tested as a reactant for butanol in the presence of advanced oxidizers. The blocking agent, p-chlorophenol, drops off at 60°C and reaction of the butanol with the isocyanate was noted. The study to determine the variables affecting the reaction of blocked isocyanates was continued with screening of a series of chloro-substituted phenols and trifluoroethanol as blocking agents. The effect of tin curing catalyst on the reactions of blocked isocyanates was investigated. The conclusions were made that the technique is feasible and that carbamates which dissociate at lower temperatures (30-40°C) would be better because there is some inhibition of dissociation by the oxidizer.

L. A redirection of the program has been made with two main objectives; one, the rapid utilization of the current technology to produce and test a propellant with wide temperature range of operation and two, the development of an energetic HAP propellant utilizing an isocyanate curing system. This report precedes the redirection effort and contains only a few of the results obtained under the new plan.

IV. TECHNICAL DISCUSSION

A. TASK ONE

1. Introduction

As a result of discussions with Mr. Robert Corley of the Rocket Propulsion Laboratory, a redirection of this task has been instituted. The objectives are to convert the technology developed by the program thus far into a propellant suitable for both tactical and ICBM motors. This involves the use of partially saturated prepolymers to achieve adequate low temperature properties and chemical stabilization of the propellant for high temperature application. To further these objectives, Mr. E. Mastrolia was assigned direction of this task. The program he will implement as of March 1 is shown in detail in Figure 1. The data reported here do not as yet include results obtained under Mr. Mastrolia's direction, but these will appear in subsequent reports.

2. Characterization of Ingredients

a. Antioxidant

The decision to utilize partially saturated prepolymers to prepare propellants with low temperature properties adequate for tactical motors, requires knowledge of the relative oxidative stability of unsaturated, partially saturated, and saturated prepolymers. The Prepolymers 242AM-169, 3HPL-123, and 3HPL-125 are admirably suited for such a study since their degrees of saturation are 0, 60, and 93%, respectively, and all have the same backbone structure and same approximate molecular weight (see AFRPL-TR-68-9). Since only their antioxidant contents were in doubt, this was determined. The antioxidant contents of a related pair of prepolymers, 242AM-175B (0% saturated) and 3HPL-90 (55% saturated) were also determined.

The determination of Antioxidant 2246 involved comparison of the ultraviolet spectrum of the prepolymer in a basic solvent in the region 275 to 400 $m\mu$ with that of a standard solution of the antioxidant. The band peak occurs at 320 $m\mu$. The results of the analyses are given in Table I.

ADVANCED HYDROCARBON BINDER PROGRAM MILESTONE SCHEDULE

Task	Feb				March				April				May			
	4	11	18	25	3	10	17	24	31	7	14	21	28	5	12	19
I. NH_4ClO_4 Propellants																
A. Complete Telagen S Evaluation																
1. Prepare and Test 88% Solids Propellants with LHT-240																
a. Uniaxial Tensile Properties																
b. Oxidative Stability (Hardness)																
c. Thermal Cycling Characteristics																
2. Compare Oxidative Stability of Propellants Prepared with Saturated, Partially Saturated (55%) and Unsaturated Prepolymers																
3. Determine effect of Bonding Agent Level in 88% Solids Propellants																
a. OTI-Cured																
b. LHT-240 Crosslinker																
4. Evaluation of "Difunctional" Telagen S																
a. End Group Analysis and Molecular Weight																
b. Prepare and Test 100g Batches of 88% Solids Propellant																
c. Prepare and Test 1-lb Batch of Optimum Composition																
B. Evaluation of Partially Saturated Prepolymers																
1. Currently Available Prepolymers																
a. Preliminary Evaluation of Oxidative Stability of Partially Saturated Prepolymers (180°F)																
(1) Binders																
(2) Propellants																
b. Strain Cylinder Evaluation of 88% Solids Propellants (15 and 20% Strain)																
(1) Measure Uniaxial Tensile Properties between -75 and +180°F																
(2) Three Cycles Between +110°F and -75°F																
(3) Three Cycles Between +180°F and -75°F																

A

HYDROCARBON BINDER PROGRAM MILESTONE SCHEDULE

Week Ending																			
March					April					May					June				
3	10	17	24	31	7	14	21	28		5	12	19	26		2	9	16	23	30

July					Aug					Sept				
7	14	21	28		4	11	18	25		1	8	15	22	29

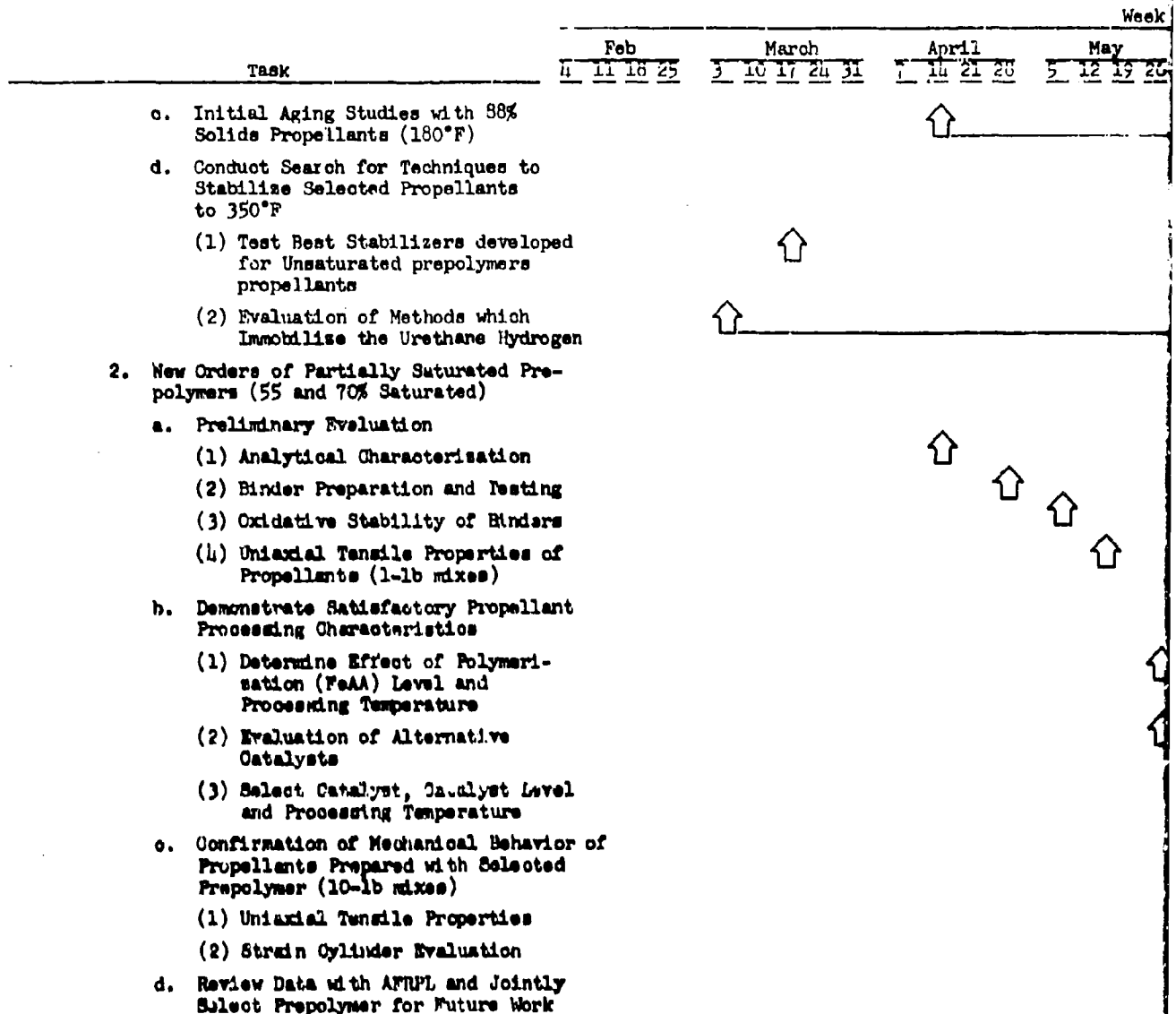


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Figure 1

B

ADVANCED HYDROCARBON BINDER PROGRAM MILESTONE SCHEDULE



A

Week Ending																															
March					April				May				June				July				Aug				Sept						
<u>3</u>	<u>10</u>	<u>17</u>	<u>24</u>	<u>31</u>	<u>7</u>	<u>14</u>	<u>21</u>	<u>28</u>	<u>5</u>	<u>12</u>	<u>19</u>	<u>26</u>	<u>2</u>	<u>9</u>	<u>16</u>	<u>23</u>	<u>30</u>	<u>7</u>	<u>14</u>	<u>21</u>	<u>28</u>	<u>4</u>	<u>11</u>	<u>18</u>	<u>25</u>	<u>1</u>	<u>8</u>	<u>15</u>	<u>22</u>	<u>29</u>	

Figure 1 (cont.)

Task	Feb				March				April				
	4	11	18	25	3	10	17	24	31	7	14	21	28
e. Confirm Aging Characteristics with Selected Stabilizers (180°F and 350°F)													
(1) Bulk Stability (Uniaxial Tensile Measurements)													
(2) Surface Stability (Hardness and Crosslink Density)													
f. Prepare 60-lb Mix and Conduct Detailed Characterisation of Propellant													
(1) Prepare 60-lb mix													
(2) Mechanical Failure Envelope													
(3) Strain Cylinder Evaluation													
(4) Bonding Properties													
(5) Aging													

II. HAP Propellants

A. Telogen S and Solid Isocyanates

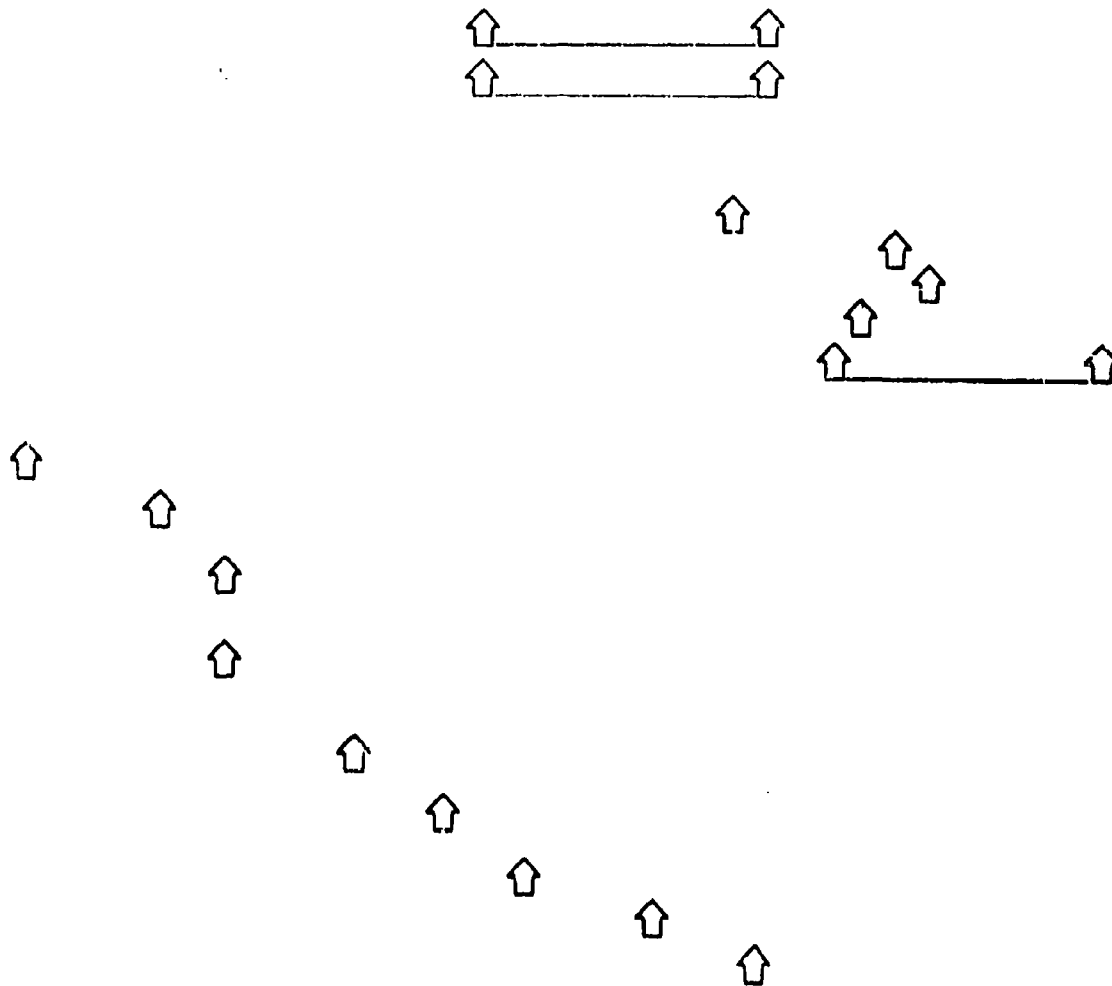
1. Isocyanate Type and Level
2. Evaluation of Selected Bases to Extend Potlife
3. Measure 77°F Tensile Properties of Selected Propellant

B. Telogen S and Blocked Isocyanates

1. Model Compound Study to Select Desired Block and Propellant Processing and Cure Temperature
2. Preparation and Evaluation of Practical Blocked Isocyanate (difunctional)
3. Evaluate Selected Blocked Isocyanate in Binders
4. Prepare and Test 85% Solids Propellants (50-100g mixes)
5. Scaleup to 1-lb Mixes
6. Aging at 77°F and 135°F

ED HYDROCARBON BTNDER PROGRAM MILESTONE SCHEDULE

Week Ending																															
March						April				May				June				July				Aug				Sept					
25	3	10	17	24	31	7	14	21	28	5	12	19	26	2	9	16	23	30	7	14	21	28	4	11	18	25	1	8	15	22	29



B

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Table I

ANTIOXIDANT CONTENT OF TELAGEN REPOLYMERS

<u>Prepolymer</u>	<u>Saturation, %</u>	<u>Antioxidant, Wt%</u>
242AM-169	0	0.10
3HPL 123	60	0.10
3HPL-125	93	0.10
242AM-175B	0	0.06
3HPL-90	55	0.04

b. Polyisocyanates

1) Mobay E-246

Mobay E-246, a polyfunctional aromatic isocyanate was slowly cooled down below its melting point to about 10°F. When the material was allowed to return slowly to room temperature, solid and liquid phases appeared. After separation and analysis, the two phases gave approximately the same equivalent weight by the dibutylamine method. The infrared spectra (Figure 2) showed no major differences in the two phases. Molecular and equivalent weights for E-246 as received and as separated, are shown in Table II.

Table II

MOLECULAR AND EQUIVALENT WEIGHT OF TREATED AND
UNTREATED MOBAY E-246

	<u>Untreated</u>	<u>Treated</u>	
		<u>Solid</u>	<u>Liquid</u>
Equivalent Wt.	136	131	131
M.W. (VPO)	366	505	364
Functionality	2.69	3.86	2.78

2) Upjohn PAPI

Upjohn PAPI, a polyfunctional aromatic isocyanate, is a dark liquid with a VPO molecular weight of 428 and equivalent weight of 139. The functionality is 3.08. Since visual observation showed that PAPI contained sediments, attempts were made to separate the latter and obtain a

INFRARED SPECTRUM OF E-24

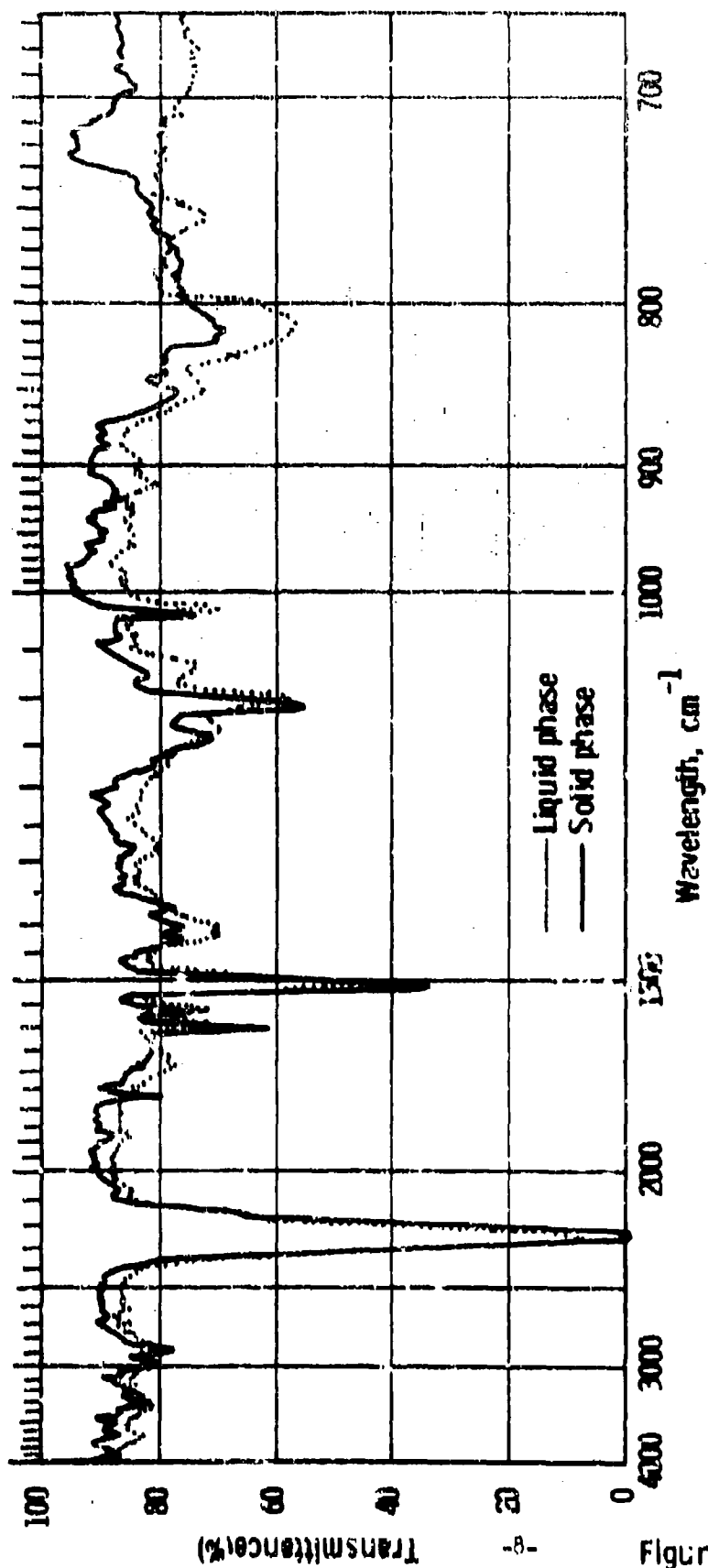


Figure 2

pure material. Fifty grams of PAPI were extracted with 2 liters of a mixture of hexane and toluene in a 90 to 10 ratio. After the solvents were evaporated, about 15 grams of straw colored product were obtained. Its equivalent weight was 134. The VPO molecular weight was 324; functionality, 2.42. Figure 3 shows the infrared spectra of as received and the extracted portion of PAPI. Interestingly, the spectrum of the purified PAPI matches that of E-246 (Figure 2). The materials must be very similar.

c. Silica Gel Chromatography

1) Experimental

Fractionation of Prepolymer 148A by column chromatography was performed to make a direct comparison between the saturated and unsaturated profiles. Prepolymer 148AH, the saturated analog of Prepolymer 148A, has already been fractionated at Aerojet and at Esso.

Following the procedure used for Prepolymers 148AH, 158H, and 161AHR, two grams of 148A were fractionated by passing it through a 7/8 inch diameter column packed with 100 g of 100-200 mesh SiO_2 . Approximately 1 liter each of CCl_4 and 2 liters of CH_2Cl_2 were used to elute the prepolymer from the column, and were collected in 20-ml fractions by an automatic fraction collector. The solvents were evaporated and an elution profile constructed (Figure 4).

Unlike the previous prepolymers fractionated, the elution profile of 148A shows only 2 major peaks. The samples representing these peaks were combined to give one sample for each major fraction. An infrared spectrum of each sample was obtained and by a semi-quantitative method, functional group content was determined. The first fraction (approx. 30% of the total) was monofunctional, and the second fraction (approx. 70% of the total) was difunctional. Contrary to the results found for the previously run prepolymers, there is no significant amount of non-functional material in 148A. Seemingly, the non-functional fraction is a result of hydrogenation. The monofunctional material is the result of the polymerization process. These results may indicate that mono-functional content is a characteristic of the available anionically derived prepolymers. This characteristic is not an inherent one, i.e., with rigorous control of processing methods, a significant reduction in the amount of monofunctional material might be affected. Also, while these results were obtained for a hydroxy-terminated prepolymer, a similar high monofunctional content may be present in carboxy-terminated prepolymers. The limitations of this study do not allow an estimate of the monofunctional content of prepolymers made by free-radical polymers. There is, however, little reason for optimism on this point because the sensitivity of free-radical polymerizations to trace impurities and to chain-transfer reactions is well known.

These shortcomings are reasons for constant, intelligent surveillance of these materials and for helpful discussions with manufacturers to facilitate progress towards improvement of materials. Historically, steady progress to improved propellant ingredients has followed the demand for such ingredients.

INFRARED SPECTRUM OF PAPI

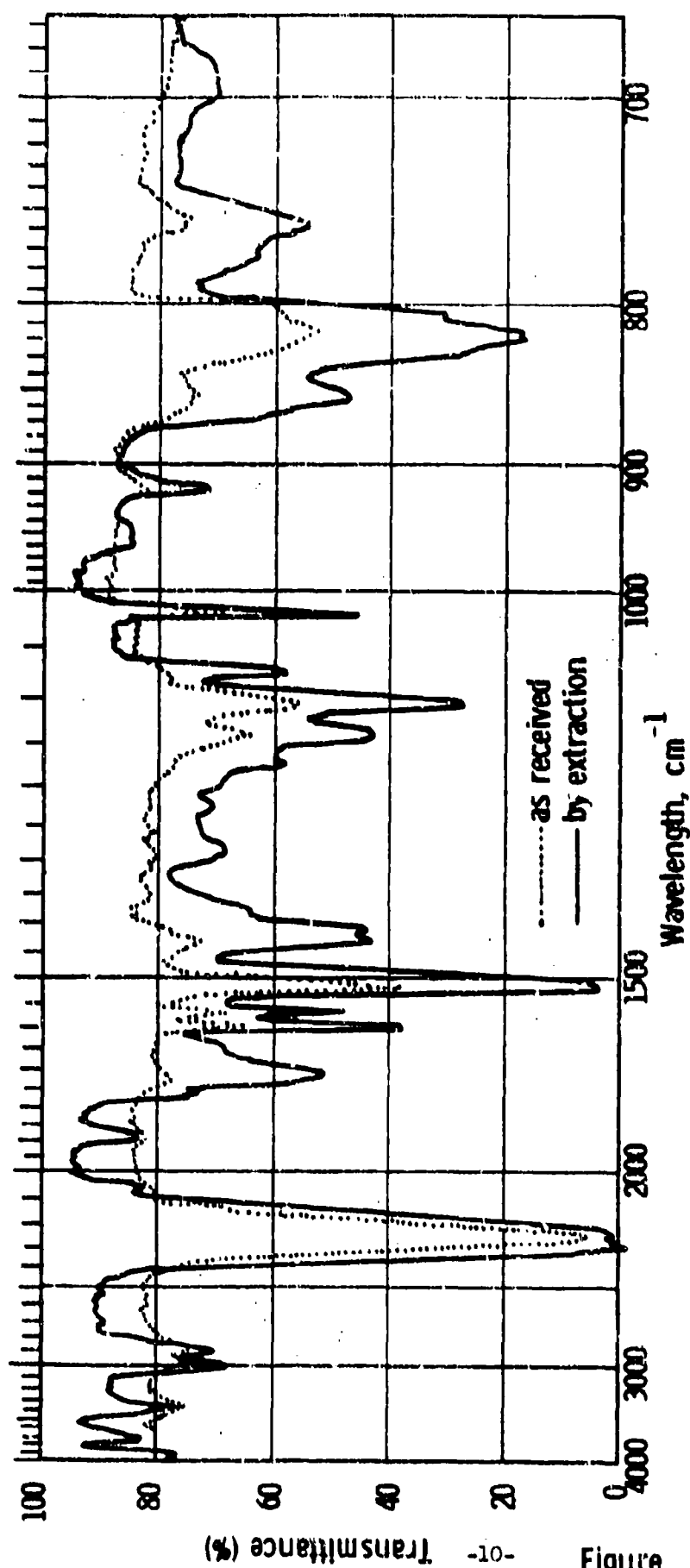
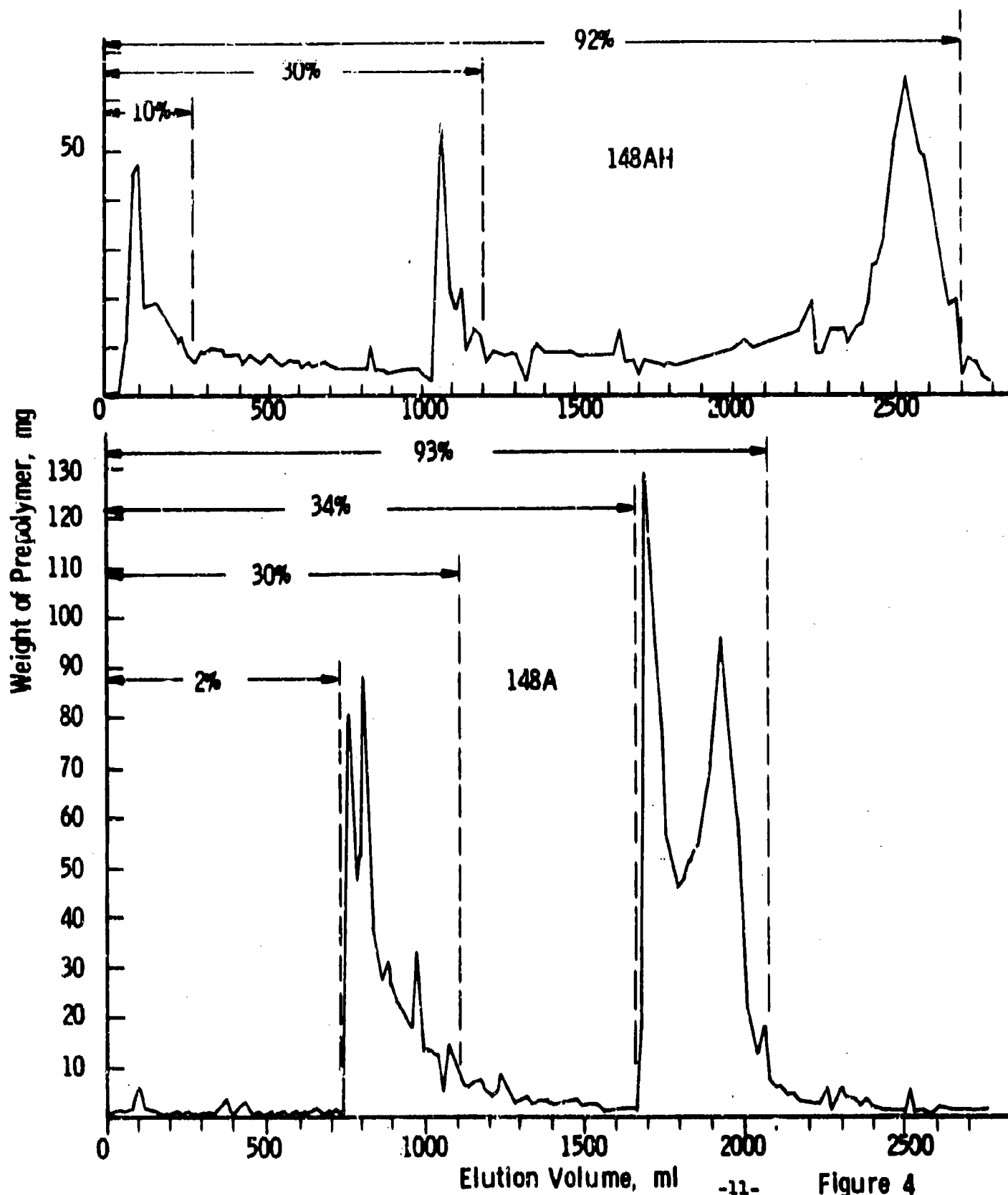


Figure 3

CHROMATOGRAPHIC FRACTIONATION OF PREPOLYMERS
148A AND 148AH ON SiO_2



2) Preparative

A chromatographic column, 95 cm long and 10 cm diameter, was filled to a depth of 45 cm with 2.5 lb of silica gel (Baker reagent grade powder for chromatography) with chloroform as the liquid phase. A solution of 50 grams of prepolymer (158H) in 50 grams of warm carbon tetrachloride was added slowly to the top of the column. After the addition of the prepolymer solution was complete, development of the column was made with chloroform at a rate of one liter per hour. The difunctional prepolymer began to elute from the column after 6 to 6.5 liters of solvent had been collected and elution was completed after 9.5 liters had been collected. An unidentified carbonyl containing compound was eluted in the small amount of materials collected beyond 9.5 liters. The total yield of difunctional prepolymer from 11 runs was 83 grams.

The functionalities of the fractions were determined from the ratios of intensities of the hydroxyl band (3330 cm^{-1}) to those of the CH bands at 1460 cm^{-1} and 1380 cm^{-1} . Prepolymer 158H with a functionality of 1.68 was the standard from which the expected relative intensities for a given functionality of the fractions were determined (Table III).

RELATION OF RELATIVE INTENSITIES OF INFRARED BANDS
TO MONO- AND DI-FUNCTIONALITY FOR PREPOLYMERS 158H

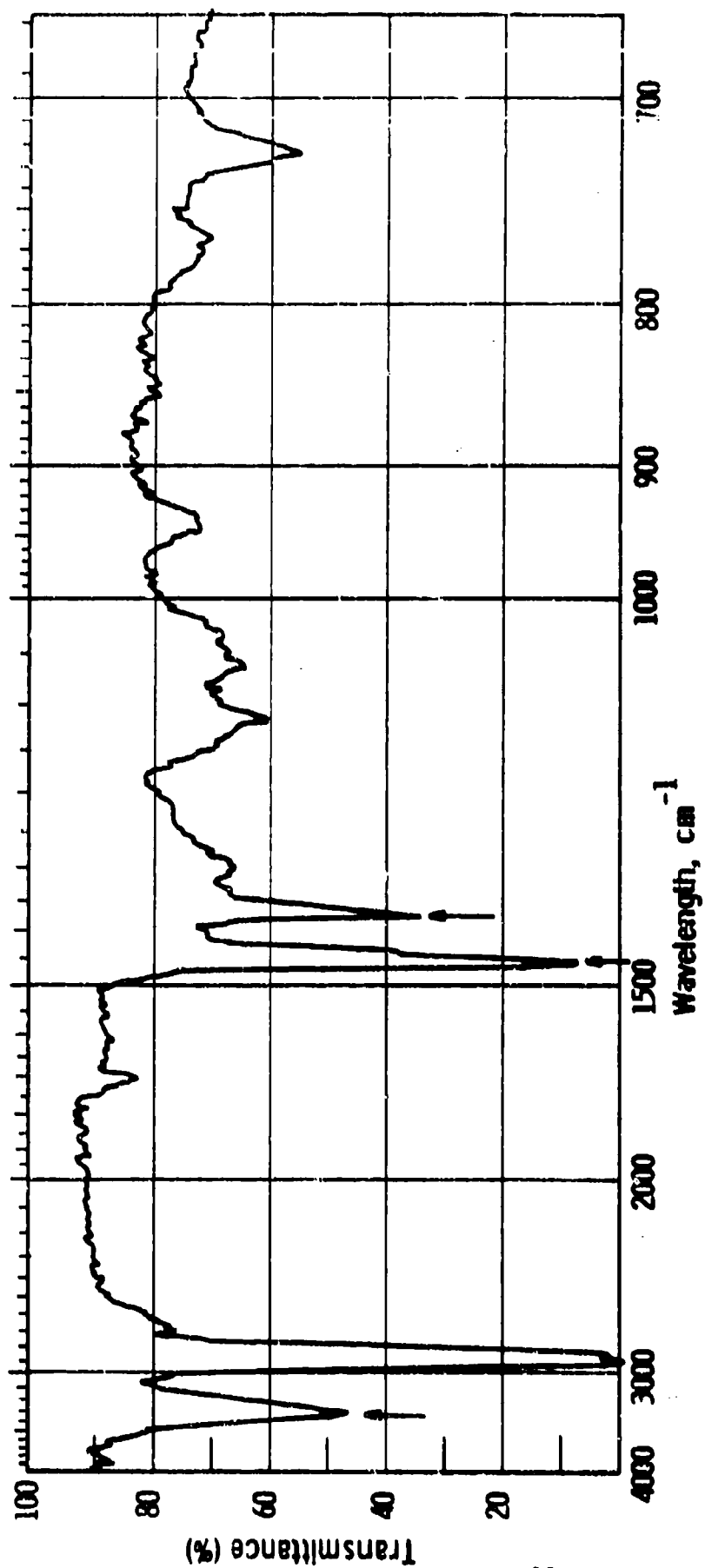
<u>Functionality</u>	<u>Expected Relative Intensities</u>	
	<u>3330/1460</u>	<u>3330/1380</u>
1	0.212	0.446
2	0.425	0.895

The OH band at 2940 cm^{-1} could also have been used for this determination, but it is so intense relative to the CH band that two solutions of proper concentration would have been required for the Perkin-Elmer laboratory instrument used for this study. By this method the functionality of the separated material was 1.93 and its infrared spectrum is shown in Figure 5.

The difunctional prepolymer which was separated was used for propellant studies, but because of the small amount of available material, no binders were made. A 100-g batch of propellant (88 wt% solids, 3% IDP) was made with the material using an HDI to CTI ratio of 3.0. The properties of this propellant at ambient temperature were $\sigma_c = 194\text{ psi}$, $\epsilon = 15\%$, and $E = 1449\text{ psi}$. Based upon these results, another 100-g batch was made at an HDI to CTI ratio of 5.0, but the propellant did not cure.

The remaining polymer was then used to prepare a 400-g batch at an HDI to CTI ratio of 3.5. For unknown reasons the modulus of this propellant was very high. The properties were σ_c , 231 psi; ϵ , 7.4%; and E , 3620 psi at 77°F and σ_c , 966 psi; ϵ , 3.6%; and E , 37300 psi at -75°F .

INFRARED SPECTRUM OF FRACTIONATED PREPOLYMER 158H
(Arrows show bands used for calculating functionality)



Whether difunctional prepolymer would result in good low temperature properties is not adequately answered by this experiment. A propellant made from conventional Prepolymer 158H with a modulus of about 3600 will be tested at -75°F and the resulting data may allow a significant comparison for determining the effect of functionality on low temperature properties.

3. Low Temperature Binder Properties

While experiments were made to assess cure capability at room temperature, the effect of primary hydroxy groups, unsaturation, and replacement of CTI by OTRO on the low temperature properties of binders was also investigated. The composition and mechanical behavior of the binders are given in Table IV.

The following conclusions were drawn from the data in Table IV.

a. Saturated, primary hydroxy terminated prepolymers produce binders which have poor low temperature properties.

b. The replacement of CTI by OTRO does not improve the low temperature behavior of saturated and partially saturated binders and may even make the low temperature properties worse.

c. As has been indicated by previous experiments, partially saturated binders have better low temperature properties than saturated ones regardless of whether CTI or OTRO is used as the crosslinker.

Mechanical properties of binders made with 3HPL-90 (55% saturated, secondary OH) and 242AM-168H (saturated, primary OH) crosslinked with CTI and OTRO followed the usual pattern. The binders (Table IV) made with 242AM-168H (Binder 262), crosslinked with CTI and tested at -40°F gave an initial modulus of 680 psi compared to 110 psi for a binder made with 3HPL-90 (Binder 270). Similar binders crosslinked with OTRO with Prepolymer 242AM-168H gave an initial modulus at -40°F of 808 psi (Binder 266) compared to 88 psi for Prepolymer 3HPL-90 (Binder 274).

Room temperature cures were obtained with both saturated and partially unsaturated prepolymers. The binders with the saturated prepolymer, 242AM-168H, which contains primary hydroxyl groups, were cured with CTI or OTRO as a crosslinker at 77°F within six days. Binders from the partially unsaturated prepolymer, 3HPL-90, with secondary hydroxyl groups cured with CTI at a slower rate (compare Binders 262 and 270, Table IV) than the binders made with the primary hydroxy-terminated Prepolymer 242AM-168H. Binders 270 and 271 with 3HPL-90, crosslinked with CTI were too soft to take penetration readings after 6 days at 77°F, but gave good penetration readings within 12 days. An adequate cure was also obtained in 6 days with 3HPL-90, crosslinked with CTI by increasing the FeAA concentration from 0.0124 to .0625 wt% (compare penetration readings for Binders 272 and 273 with those for 270 and 271 in Table IV). Binders crosslinked with OTRO and containing 3HPL-90 (274 to 277) were too soft to permit penetration readings after six days at 77°F. This was expected since OTRO contains highly hindered secondary hydroxyl groups.

Table IV

COMPOSITION^a AND PROPERTIES OF TELADEX S BINDERS

Reference No.	Prepolymer	Cross- linker	HDI/CTI	Extent of Cure Penetration		Mechanical Properties			
				Reading at 15 sec		Temp °F	E _o psi	Mooney-Rivlin	
				Days at 77°F				0 ₁ Kg/Cm ²	0 ₂ Kg/Cm ²
				6	12				
262	242AM-168H	CTI	4.00	.898	.907	77 -40	21 680	0.094 2	0.2 12
263	242AM-168H	CTI	3.75	.898	.917	77 -40	29 623	0.183 3.7	0.2 5.6
264	242AM-168H	CTI	3.50	.890	.916	77 -40	38 580	0.273 3.1	0.2 8.0
265	242AM-168H	CTI	3.00	.908	.917	77 -40	39 656	0.264 3.0	0.2 6.6
266	242AM-168H	OTRO	4.00 ^b	.888	.903	77 -40	19 808	0.079 1.9	0.1 11.4
267	242AM-168H	OTRO	3.75 ^b	.898	.907	77 -40	12 765	0.095 2.50	0.1 10.0
268	242AM-168H	OTRO	3.50 ^b	.901	.909	77 -40	21 590	0.101 2.50	0.1 9.0
269	242AM-168H	OTRO	3.00 ^b	.887	.890	77 -40	15 765	0.038 2.7	0.1 8.6
270	3HPL-90	CTI	4.00	- ^a	.890	77 -40	11 110	0.037 0.20	1.2 0.7
271	3HPL-90	CTI	3.75	- ^a	.898	77 -40	16 110	0.64 2.75	0.1 0.9
272	3HPL-90	CTI	3.50	.893	.897	77 -40	13 88	0.045 0.35	0.1 0.6
273	3HPL-90	CTI	3.00	.916	.917	77 -40	24 93	0.104 0.52	0.1 0.6
274	3HPL-90	OTRO	4.00 ^b	- ^a	.860	77 -40	8 98	0.01 0.180	0.0 0.7
275	3HPL-90	OTRO	3.75 ^b	- ^a	.865	77 -40	9 93	0.015 0.25	0.0 0.7
276	3HPL-90	OTRO	3.50 ^b	- ^a	.885	77 -40	13 82	0.029 0.25	0.0 0.6
277	3HPL-90	OTRO	3.00 ^b	- ^a	.883	77 -40	13 110	0.033 0.37	0.1 0.6

^aAll binders have an NOO/OH ratio of 1.00 and 25% IDP. Binders 262 through 271 contained 0.6^bPrepolymer to OTRO ratio.^cToo soft to take readings.

Table IV

POSITION^a AND PROPERTIES OF TELAGEN S BINDERS CURED AT 77°F

At of Cure Position at 15 sec at 77°F	Mechanical Properties				Crosslink Density 10 ⁸				Ratio of Mech. Prop. -40 to 77°F	
	Temp °F	E _o psi	Mooney-Rivlin		Gel Fraction	Gel Fraction	C ₁	Compression Modulus	C ₁	E _o
			C ₁ Kg/Cm ²	C ₂ Kg/Cm ²						
.907	77 -40	21 680	0.094 2	0.152 12	.042	0.50	0.94	0.70	21	24
.917	77 -40	29 623	0.183 3.7	0.172 5.6	.062	1.20	1.8	1.25	21	22
.916	77 -40	38 580	0.273 3.1	0.260 8.05	.077	1.80	2.73	1.09	11	15
.917	77 -40	39 656	0.264 3.0	0.198 6.6	.071	1.50	2.64	1.05	11	17
.903	77 -40	19 808	0.077 1.9	0.134 11.4	.037	0.40	0.79	0.66	24	43
.907	77 -40	19 765	0.095 2.50	0.128 10.0	.043	0.50	0.95	0.98	26	40
.509	77 -40	21 590	0.101 2.50	0.148 9.0	.044	0.50	1.01	0.61	25	28
.390	77 -40	15 765	0.038 2.7	0.113 8.6	.042	0.50	0.38	0.54	73	51
.890	77 -40	11 110	0.037 0.20	1.09 0.72	.026	0.20	0.37	0.44	5	10
.890	77 -40	16 110	0.64 2.95	0.114 0.90	.032	0.30	0.64	0.53	5	7
.897	77 -40	13 88	0.045 0.35	0.10 0.64	.025	0.20	0.45	0.31	8	7
.917	77 -40	24 93	0.104 0.52	0.186 0.60	.046	0.64	1.04	0.74	5	4
.860	77 -40	8 88	0.01 0.180	0.062 0.75	-	-	0.100	-	18	11
.865	77 -40	9 93	0.015 0.25	0.069 0.73	-	-	0.15	0	17	10
.885	77 -40	13 82	0.029 0.25	0.094 0.62	.028	0.25	0.29	0.36	9	6
.888	77 -40	13 110	0.033 0.37	0.104 0.69	-	-	0.33	-	8	11

DP. Binders 262 through 271 contained 0.0104% FeAA; the rest had 0.0625%.

A more sensitive hardness test to determine when binders have reached a steady state of cure was evaluated. A thickness gage, consisting of a 3-oz weight on top of a deflection (.001") gage, attached to a small rod with a disc at the bottom was used to get penetration readings from the binder samples. After the 3-oz weight on the sample had been released for 15 sec, a reading was recorded. After these readings became constant for several days, the sample was considered cured.

The results indicate that a partially saturated prepolymer similar to 3HPL-90 but with primary hydroxy groups would be desirable for room temperature cure. The crosslink densities obtained from the C_{cl} gel fraction and compression modulus indicate that Prepolymer 242AM-168H gives a higher degree of crosslinking than does 3HPL-90 with CTI or GTRO. This could be explained by the fact that 168H has a practical functionality of 1.96 compared to 1.90 for 3HPL-90. The processing properties of propellant with 88% solids at room temperature would also be improved if the prepolymer having primary hydroxyl had a lower viscosity, similar to that of 3HPL-90.

4. Low Temperature Propellant Properties

One pound batches of propellants containing Prepolymers 242AM-169, 3HPL-123, and 3HPL-125 were prepared with CTI and HDI for evaluation of low temperature properties. Batches 10P-4881, 4882 and 4883 (Table V) had mechanical properties that followed the same basic pattern of previous prepolymers. Batch 10P-4881 with 3HPL-125 (93% saturated) had an initial modulus at -75°F of 41,500 psi, compared to 15,900 psi for Prepolymer 3HPL-123 with 60% saturation. Although the propellants were crosslinked with CTI, previous results indicate that the low temperature properties are independent of the type of crosslinker and depend mainly on the degree of unsaturation.

Propellant batches containing Prepolymer 3HPL-90 (54% saturated) linked with Mobay E-246 (batches 6, 7, 5416) gave good mechanical properties at both 77° and -75°F. The propellants were cured by a method which ensures long potlife. The method developed by Dr. Oberth on an IR&D program consists of the incorporation of a curing aid in the propellant system with an excess of isocyanate. These propellants were designed so that the FeAA-catalyzed hydroxyl-isocyanate reaction is essentially completed before crosslinking occurs. These particular propellant formulations contained an NCO/CH equivalents ratio of 1.35. The initial modulus of this system is acceptable, but could be lowered by increasing the HDI to E-246 ratio or by decreasing the total equivalents of isocyanate. These results indicate that Mobay E-246 is a good candidate for the replacement of CTI.

Propellants prepared for an Aerojet-General IR&D program and containing a partially saturated prepolymer and the crosslinker LHT-240 have shown -75°F elongations of 30% or more. This crosslinker, because it is a polyether triol (molecular weight 750), was not used with hydrocarbon prepolymers on this program. Table VI shows the ambient and low temperature properties of propellants made with this crosslinker. The LHT-240 replaced the CTI to maintain the crosslink density constant and the HDI was adjusted to maintain the NCO to CH ratio at 1.02.

Table V

COMPOSITION^a AND PROPERTIES OF PROPPELLANTS PREPARED WITH TRIACEN 3 PRE POLYMERS

Reference No. IGP-	Composition Prepolymer ^c HDL/CTI	Cure, days at 135°F	Hardness ^b Shore A Top Side	Mechanical Properties								E, 150°F E, 77°F	
				Temp °F	% psi	% psi	% psi	% psi	% psi	% psi	E, psi		
4881	3HPL-125	3.75	30 43	77 -40 -75	81 690 1061	79 680 998	32 7 4	32 7 4	32 7 4	32 7 4	346 13,834 41,491	120	
4882	242AM-169	3.00	70 69	77 -40 -75	186 536 778	186 530 778	19 17 8	19 17 8	19 17 8	19 17 8	1,251 5,394 15,701	13	
4883	3HPL-123	3.67	43 45	77 -40 -75	90 385 775	90 350 769	41 17 8	41 17 8	41 17 8	41 17 8	378 4,586 15,920	45	
4920R	3HPL-90	5.00	49 57	77 -40 -75	89 470 699	83 439 688	49 18 9	49 18 9	49 18 9	49 18 9	459 4,892 12,950	28	
4921R ^d	3HPL-90	5.00	24 35	77 -40 -75	44 361 699	42 287 690	29 15 8	29 15 8	29 15 8	29 15 8	356 5,405 15,112	42	
6	3HPL-90	4.00 ^e	83 76	77 -75	135 759	126 752	37 8	37 8	37 8	37 8	758 17,164	23	
7	3HPL-90	3.00 ^e	79 76	77 -75	137 742	126 735	41 8	41 8	41 8	41 8	758 15,537	21	
5416	3HPL-90	2.00 ^e	80 83	77 -75	78 755	68 755	35 6	35 6	35 6	35 6	364 19,086	54	

^aAll propellants contained 58% solids, 3% IGP, C-1, HAA, Fema with a NCO/OH ratio of 1.62 except 6, 7, and 5416 (NCO to OH = 1.25).

^bFifteen-second readings. Saturation levels are 242AM-169, 48; 3HPL-90, 546; 3HPL-123, 608; 3HPL-125, 938. C-1 replaced with TEPAN. HDI to E-246 ratio.

Table VI

COMPOSITION^a AND PROPERTIES OF PREPOLYMERIS WITH TELAMER 3 PREPOLYMERIS CROSSLINKED WITH LHT-21.0

Reference No. IGP-	Prepolymer	Degree of Saturation %	Crosslinker	Hardness Shore A		Mechanical Properties									
				Top	Bottom	Temp °F	σ _a psi	σ _b psi	ε _a %	ε _b %	σ _b psi	E _a psi	E _b psi	E _a -75°/°F	E _b -75°/°F
5597	MEPL-125	93	CTI(control)	80	82	77 -75	237 1787	224 1643	23 2	24 2	1,123 76,387			58	
5598	MEPL-125	93	DET-240	35	47	77 -75	65 1247	54 1296	37 3	44 3	258 53,087			21	
5580	MEPL-123	60	CTI(control)	62	74	77 -75	139 766	129 757	30 5	33 6	632 19,545			31	
5583	MEPL-123	60	DET-240	51	59	77 -75	79 906	69 536	40 4	42 4	764 31,992			42	
5596	MEPL-90	55	DET-240	53	61	77 -75	84 737	72 660	39 7	43 16	716 16,793			23	

^aAll prepolymers contain 88% solids, 3 wt% DET, C-1, HAA, PMA with an HCO/OH ratio 1.02 and were cured 7 days at 135°F

The properties do not indicate a significant advantage for the LHT-240. However, since the propellant properties obtained on the IR&D program have been consistently good, further work in this area is necessary. The formulations developed by the IP&D group differ from those given here by using TDI instead of HDI and 35% dioctyl sebacate instead of 25% IDP.

The original saturated hydrocarbon propellant developed on this program included diethanolamine (DEA) as a bonding agent, but the use of this material was later abandoned because it was shown to increase the propellant crosslink density. While tests of other bonding agents were made, C-1 has remained the favored one; the work to date has been mainly with 0.1 wt% of this bonding agent. Table VII indicates the effect of increased concentrations of the C-1 bonding agent on the propellant properties at -75°F.

Table VII

**EFFECT OF C-1 ON MECHANICAL PROPERTIES OF
PARTIALLY SATURATED TELAEN PROPELLANTS^a**

Reference No.	C-1 Wt%	Hardness Shore A		Mechanical Properties						
		Top	Bottom	Temp °F	E ₁₀ psi	E ₁ psi	e ₁₀ %	e ₁ %	E ₀ psi	E ₀ -75°F/ E ₀ -77°F
9	.10	69	66	77 -75	129 704	117 692	42 9	50 13	616 14,784	24
18	.20	62	60	77 -75	120 719	110 719	37 9	42 10	631 13,823	22
19	.30	70	55	77 -75	71 710	65 719	41 11	47 16	371 12,775	24

^aAll propellants contain 88% solids, Prepolymer JHPL-90, 3 wt% IDP, HAA, FeAA, a NOO/H ratio of 1.02 and were cured 7 days at 135°F.

The low temperature mechanical properties show improvement with increased amounts of C-1. The results are somewhat ambiguous because the propellant with the best low temperature properties also showed the lowest ambient temperature modulus and tensile strength. These results, however, will be used in guiding the formulation of future propellants. If propellants stable at temperatures above 180°F are desired, the bonding agent, C-1, will have to be replaced as it decomposes at high temperature. Bonding agents suitable for use at high temperature are available.

Data in Table V for propellant batches 10P-492CR and 492IR indicate that no improvement in mechanical properties at low temperature was attained when C-1 was replaced with TEPAN. The bonding agent, TEPAN, has an equivalent weight of 170.

5. Effect of Prepolymer Saturation on Binder Aging

Aging studies have been made to determine the effect of oxidative crosslinking on binders prepared from prepolymers with various degrees of unsaturation. The samples were aged at 80°C in a circulating air atmosphere along with control samples sealed in ampules having an argon atmosphere. The samples were studied by a micro-swelling technique to determine the extent of oxidative effects. The results are given in Table VIII and Figure 6.

Thin sections were microtomed perpendicular to the surface and swollen. The samples which hardened at the surface swelled very little at the surface and more as the distance from the surface increased. The hardened surface became bowed and constrained the swelling of binder adjacent to it. Under polarized light the hardened surface was birefringent and the depth of the hardened portion could be easily measured.

The surface of all binders (except Binder 245) hardened after 4 weeks storage at 80°C in air. Binder 245 containing 3HPL-125 (93% saturation) was the only binder whose surface could be swelled with toluene after 4 weeks in air at 80°C. Samples stored in argon exhibited no change in surface hardness. The extent of the increase in the hard surface caused by oxidative crosslinking of the double bonds is shown in Figure 6.

The initial data indicated that surface hardening may be more rapid in the partially saturated binders. Because there may be several explanations (loss of antioxidant effectiveness on hydrogenation, effect of traces of hydrogenation catalysts), the effect was examined more closely.

After eight weeks, samples indicated that surface hardening of binders with unsaturation (Table VIII and Figure 6) was continuing, but that the differences in degree of hardening between the samples decreased. The unsaturated prepolymer was hardening at the fastest rate. The binder prepared with the saturated prepolymer showed no surface hardening.

A new set of binders for aging studies was prepared with two sets of unsaturated prepolymers and partially saturated prepolymers obtained by the hydrogenation of the unsaturated ones. Thus, the data will be more meaningful by comparing prepolymers from the same polymerization (174B, 0% saturated, with 3HPL-90, 54% saturated, and 242AK-169, 0% saturated, with 3HPL-123, 60% saturated). The results of one week aging (see Table VIII) essentially duplicate the results found in the first experiment.

The data obtained are extremely critical because they will decide whether partially saturated prepolymers have an advantage over unsaturated prepolymers with respect to oxidative crosslinking. The samples under study at this time together with studies of prepolymers with nominally 70% saturation, which are also planned, should give a better answer to this question.

6. Aging Stability

a. High Relative Humidity, 180°F

Both partially and completely saturated prepolymers were

Table VIII

SWELLING OF AGED TELAGEN AND

Swelling^b by T

Ref. No.	Prepolymer	% Sat.	HDI/ OTI	Initial Values			1 Week			In
				Sur- face	Sub- surface	Con- ter	Sur- face ^c	Sub- surface	Con- ter	
240R	3HPL-90	54	3.75				-	-	119	-
241R	3HPL-90	54	3.50				-	-	111	-
242R	3HPL-90	54	3.00				-	108	108	-
245	3HPL-125	93	3.50				103	-	-	114
250	3HPL-123	60	3.00				113	113	97	-
252	242AM-169	0	3.75				-	77	90	-
253	242AM-169	0	3.50				74	78	89	-
254	242AM-169	0	3.00				98	98	98	-
257	3HPL-90	54	2.00 ^d				-	89	105	-
260	3HPL-90	54	3.00 ^e				-	104	114	-
288	3HPL-90	54	3.00	111	-	110	-	87	107	
289	3HPL-123	60	3.00	102	-	96	-	100	96	
290	242AM-169	0	3.00	108	-	114	-	98	77	
291	174-B	0	3.00	128	-	136	-	88	116	

^aBinders have NCO to OH equivalents ratio of 1, 25% IDP, and .0312% FeAA. They were cured by change in length after swelling in toluene, $100[(L - I_0)/L_0]$.

^cWhen value not given there was a hard brittle surface layer which did not swell.

^dHDI/PAPI

^ePrepolymer/OTRO.

Table VIII

AGED TELAGEN AND TELAGEN S BINDERS

Swelling^D by Toluene After Storage at 80°C

k	In Air						In Argon					
	2 Weeks			4 Weeks			8 Weeks			4 Weeks		
ce	Center	Sur-face ^c	Sub-surface	Center	Sur-face ^c	Sub-surface	Center	Sur-face ^c	Sub-surface	Center	Sur-face	Center
	119	-	-	98	-	79	107	-	91	107	92	121
	111	-	90	99	-	95	101	-	82	95	84	116
	108	-	-	104	-	89	99	-	84	89	102	115
	-	114	112	117	120	113	100	115	118	118	120	108
	97	-	86	92	-	84	95	-	96	99	122	111
	90	-	83	90	-	70	91	-	78	85	115	150
	89	-	78	95	-	65	88	-	67	84	118	110
	98	-	83	90	-	58	84	-	72	84	114	112
	105	-	117	123	-	105	118	-	105	104	-	-
	114	-	98	116	-	67	122	-	88	115	102	120
	101											
	96											
	77											
	116											

AA. They were cured at 135°F for 7 days.

not swell.

B

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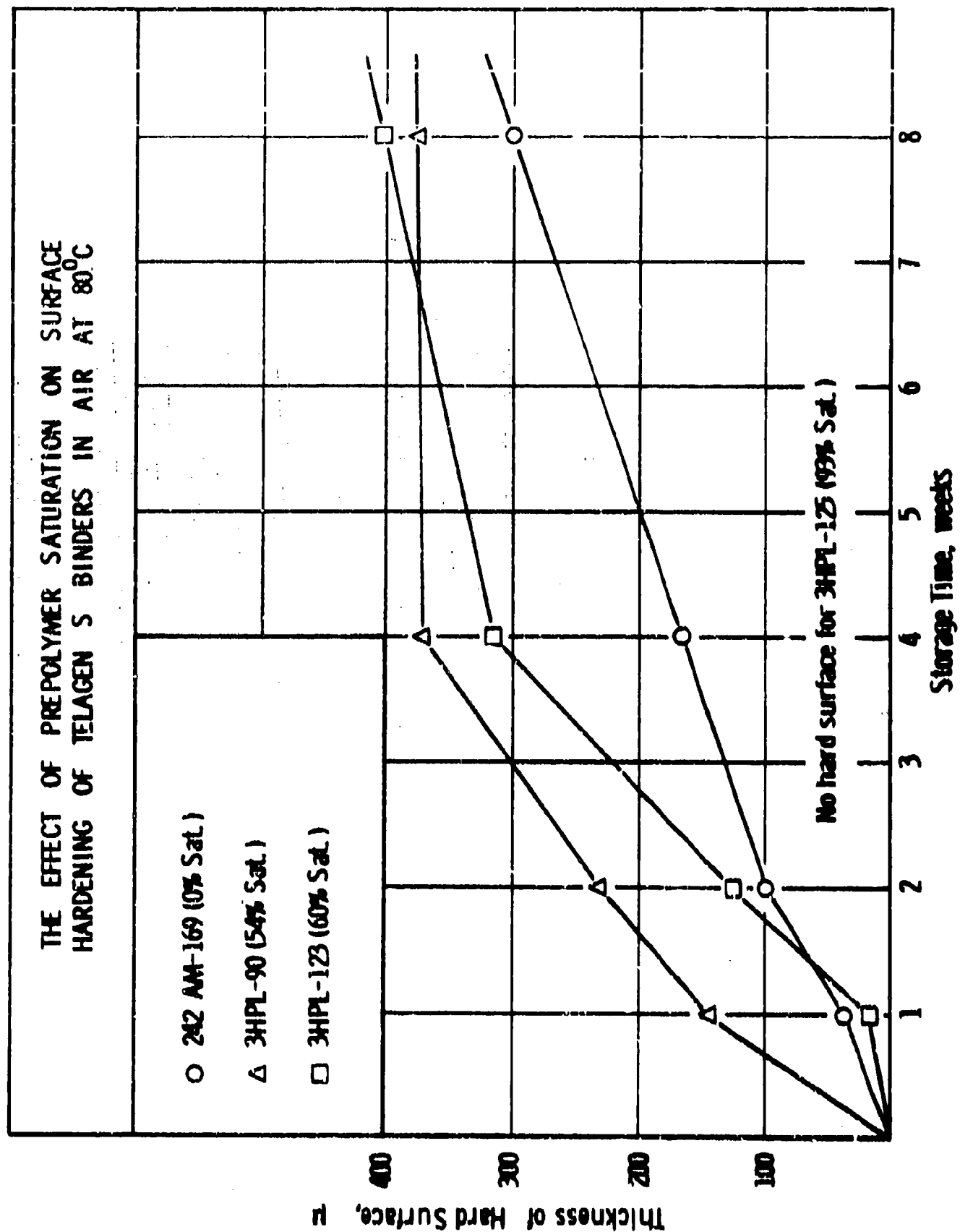


Figure 6

used to prepare propellants containing stabilizers. The saturated prepolymer based propellants showed good stability at 180°F except when exceptionally high relative humidities (25 to 80%) were encountered. These relative humidities are unnaturally high, but propellants which can survive them would be stable under actual moist environments.

Table IX shows the ambient temperature mechanical properties of stabilized, aged propellants made with a partially saturated prepolymer. Copper (II) showed promise as a stabilizer for these propellants. Table X gives the same type of data for a saturated hydrocarbon propellant. Again, copper (II) was good although oxidative crosslinking is not a problem for these propellants.

The propellants were in the form of Instron bars and stored at 50% relative humidity at 180°F. The storage time was short for this screening test, but the best stabilizers will be used for longer tests.

b. 350°F

Exploratory testing of hydrocarbon, isocyanate-cured propellants was done to determine stability at 350°F. Dr. A. E. Oberth and other Aerojet workers on an IR&D program have done experiments which indicate that stability at 350°F is attainable with isocyanate-cured propellants. Unsaturated and partially saturated prepolymers were used in the propellants which were placed in an oven at 350°F for a 2 hour period. No special oxidizer was used for these tests. The sample was an Instron bar. The results are shown in Table XI.

The general behavior of the propellants was to harden, many to the point of brittleness. This was not entirely expected since urethanes reportedly decompose at high temperature. The decomposition of the urethane was not a problem. The copper (II) stabilized propellants looked the best when examined visually after aging. This is indicated also by the data in Table XI. All samples showed signs of swelling, although in some cases only very slightly. The swelling could arise from decomposition of NH_4ClO_4 , evaporation of IDP, or decomposition of the C-1.

While these experiments were only initial attempts, they were encouraging. The data will be used for planning future experiments in high temperature stabilization.

B. TASK TWO

1. Introduction

Discussions with Mr. Corley of the Rocket Propulsion Laboratory resulted in changes in the objectives of Task Two. The current objectives are the development of an energetic isocyanate-cured MAP propellant by two approaches. One approach involves the use of blocked isocyanates as curing agents and the other, the use of low melting, solid isocyanates. This task will be directed by A. J. Di Milo. The program schedule is shown in Figure 1. Some work with HDP (done before the above discussions) is reported.

Table II

EFFECT OF STABILIZERS ON THE AGING OF PARTIALLY SATURATED PROPELLANTS^a

Batch No.	Stabilizer	Amount Wt %	Aging Time, week	Hardness Shore A 15 sec	Mechanical Properties at 77°F					
					σ_b psi	σ_t psi	ϵ_b %	ϵ_t %	E psi	E_o psi
9	None	0	0	69	129	117	42	50	616	
			1	-	78	72	20	24	736	
			2	70	76	76	9	9	1655	
10	HEMA ^b	.20	0	56	86	81	38	41	430	
	DEHT ^b	.05	1	42	50	31	37	62	394	
			2	53	60	51	22	43	562	
16	HEMA	.20	0	45	65	58	50	57	286	
	Sulfur	.10	1	37	54	38	47	70	404	
	Ca(II)	.10	2	46	59	49	40	59	443	
	DEHT	.05								
17	Ca(II)	.10	0	72	167	155	25	27	1053	
	Sulfur	.10	1	73	165	152	13	16	1813	
			2	79	128	123	10	12	1861	
20	Ca(II)	.10	0	68	156	148	34	36	740	
			1	67	156	141	27	31	924	
			2	68	124	118	24	28	870	
21	P-33	.10	0	59	138	133	25	26	925	
			1	64	69	69	2	2	5816	
			2	78	74	74	2	2	4760	

^a All propellant contain 80% solids, HPL-90, 3 wt% IDP, HAA, FeAA, with an NCO/OH ratio of 1.02 and were cured 7 days at 135°F. All were aged as Instron bars at 50% relative humidity and 180°F.

^b A radical terminator.

Table X

EFFECT OF STABILIZERS ON THE AGING OF TECAGEN 3 PROPELLANTS^a

Batch No.	Stabilizer	Amount Wt %	Aging Time, week	Hardness Shore A 15 sec	Mechanical Properties at 77°F					
					σ_b psi	σ_c psi	e_b %	e_c %	E_o psi	
12	none	0	0	45	72	72	36	41	272	
			1	61	68	52	42	58	301	
			2	40	67	58	40	51	276	
13	P-33	.10	0	43	89	80	43	48	316	
			1	42	80	64	39	51	342	
			2	44	81	69	32	46	488	
14	Cu(II)	.10	0	40	74	64	43	52	283	
			1	42	69	57	39	54	318	
			2	40	64	55	40	51	328	

^aAll propellant contain 88% solids, 161H, 3 wt% IDP, C-1, HAA, FeAA with an NCO/OH ratio of 1.02 and were cured 7 days at 135°F. All were aged as Instron bars at 50% relative humidity and 180°F.

Table XI

EFFECT OF STABILIZERS ON HIGH TEMPERATURE (350°F) AGING OF HYDROCARBON PROPELLANTS

Reference No. MCP-	Prepolymer	Degree of Saturation %	Stabilizer and Concn, Wt%	Hardness Shore A	Initial and After-Aging ^b Mechanical Properties at 77°F				
					σ_b psi	ϵ_b %	σ_a psi	ϵ_a %	E psi
5710	175B	0	Cu(II) 0.10	52	85	80	57	68	262
				-	88	88	9	9	978
5711	3HPL-90	55	Cu(II) .10	51	83	79	58	64	261
				72	122	122	14	14	1034
5712	242AB-169	0	Cu(II) .10	57	98	92	35	40	417
				80	102	102	7	7	1982
5713	3HPL-123	60	Cu(II) .10	53	93	90	34	38	406
				69	57	56	7	7	889
5714	175B	0	Cr(III) .10	53	98	94	57	61	329
				77	54	54	5	5	1235
5715	3HPL-90	55	Cr(III) .10	53	96	94	50	55	339
				57	Too brittle to measure.				
5714	175B	0	Cr(III) .30	54	101	98	43	48	381
				66	Too brittle to measure.				
5735	175B	0	Cr(III) .30	29	32	29	59	72	198
				80	97	97	8	8	1587
5736	3HPL-90	55	Cr(III) .30	48	96	90	48	52	340
				60	Too brittle to measure.				
5737	3HPL-90	55	Cr(III) .30	30	48	45	62	72	157
				60	Too brittle to measure.				

^a All propellant contain 90% solids, 3 wt% DOP, C-1, HAA, FcAA, with an NCO/OH ratio of 1.02 and were cured 7 days at 135°F.

^b Aged as Instron bars for 2 hours at 350°F.

2. Approach

The studies of the compatibility of advanced fuels and oxidizers with binder components were limited to the study of HAP and isocyanate-cured prepolymers. The prepolymers were limited to primary hydroxy-terminated ones since HAP causes dehydration of secondary hydroxyl-groups. Because isocyanate reacts rapidly with secondary alcohols and even faster with primary alcohols (in the presence of HAP) the rate of reaction must be decreased to allow sufficient pot life for propellant preparation. At present two possible methods for increasing pot life are being investigated, (a) the use of low melting isocyanates and (b) blocked isocyanates, which after propellant mixing, casting and heating to a suitable temperature, will react with the prepolymer for the cure process. The blocked isocyanates under current investigation dissociate to sufficient degree at about 60°C with or without a catalyst.

3. Blocked Isocyanates

Development of a curing system for advanced oxidizers has been mainly centered on a urethane crosslink, because isocyanates are relatively free of side reactions in the presence of oxidizers. The main problem has been concerned with decreasing the rate of reaction between the alcohol and isocyanate to a point where a reasonable pot life is attained in the presence of the oxidizer. The rate of reaction has been reduced through the use of a low melting solid isocyanate, Carwinate 125N. With this isocyanate, curing is accomplished at a temperature above the melting point of the solid isocyanate. Another technique for obtaining a slow cure is the slow release of one of the reactants from an inactive form. This technique is preferable to the use of low melting solids materials since the reactant is introduced into the reaction medium at a controllable rate. Recent studies have been concerned with blocked isocyanates which undergo thermal dissociation.

Model studies were made with phenyl isocyanate blocked with p-chlorophenol and its reaction with n-butyl alcohol in the presence of various oxidizers and a catalyst, T-20 (tin-sulfur compound). After 18 hours at 23°C, the reaction was too slow to measure unless the catalyst T-20 was present. At 80°C the reaction in the presence of HDP was too fast and considerable decomposition of the oxidizer was observed. The initial studies (Table XII) indicated that HDP may be a catalyst for the dissociation of the blocked isocyanate and that T-20 also was effective in this regard. An increase in temperature from 23°C to 60°C also had a pronounced effect on the dissociation of the blocked urethane. The formation of n-butyl N-phenylcarbamate, even though at a very slow rate, indicated that the blocked urethane is potentially useful as a source of isocyanate for the urethane cure system for advanced oxidizers.

The study was continued to find more active blocking groups and the effect of added catalysts. Model studies were made of blocked phenyl isocyanate and its reaction with n-amyl alcohol. The blocking groups investigated were 2,2,2-trifluoroethanol, 4-chloro-, 3,4-dichloro-, 2,4,6-trichloro-, and 2-chloro-4-nitrophenol. The catalysts investigated were T-20, a sulfur containing tin compound, and bis-(tri-n-butyltin)oxide (TBTO).

Table XII

THE REACTION OF p-CHLOROPHENYL N-PHENYLCARBAMATE WITH
n-BUTANOL IN THE PRESENCE OF VARIOUS OXIDIZERS AND
WITH T-20^a AT 23 and 60°C FOR 17 HRS

<u>Oxidiser</u>	<u>Temp °C</u>	<u>Catalyst</u>	<u>n-Butyl N-Phenyl- carbamate, g formed</u>
AP	23	T-20	5
HAP ^b	23	T-20	7
HDP	23	T-20	13
AP	60	none	2
HAP	60	none	1
HDP	60	none	28
none	60	T-20	10
AP	60	T-20	13
HAP	60	T-20	9
HDP	60	T-20	26

^aTin-sulfur compound.

^bHAP was impure NOB material.

The catalyst studies (Table XIII) indicated that T-20 at 0.5% by weight of organic components was a slightly better catalyst for the dissociation of 2,4,6-trichlorophenyl N-phenylcarbamate than bis-(tri-n-butyltin)oxide. Evidently, the presence of HAP either reduced the effectiveness of the catalyst or hindered the desired reaction in some other manner.

Larger amounts of catalyst (T-20) increased the amount of reaction only slightly, but not proportionate to the forty fold increase of catalyst (Table XIV). Apparently thermal dissociation of the blocked urethanes was inhibited by the presence of HAP (Table XII).

A comparison of the blocked isocyanates (Table XVI) showed that the 2,4-dichloro-, 2-chloro-4-nitro-, and 2,4,6-trichlorophenyl derivatives react more readily than the 2,2,2-trifluoroethyl or the 4-chlorophenyl derivative. Since the initial studies did not indicate any great differences in the degree of reactivity between the di- and tri-substituted phenyl derivatives, di and tri-functional isocyanates will be blocked with 2,4,6-trichlorophenol because of its lower cost.

Table XIII

CATALYTIC ACTIVITY OF T-20 AND TBTO IN THE REACTION OF
2,4,6-TRICHLOROPHENYL N-PHENYLCARBAMATE WITH n-AMYL ALCOHOL
IN BENZENE AT 60°C^a

<u>Catalyst</u>	<u>Oxidizer</u>	<u>n-Amyl Alcohol</u> <u>% remaining after 24 hr</u>
T-20	none	14.7
T-20	HAP	61.5
TBTO	none	23.6
TBTO	HAP	65.0

^aReactants conc., 0.5M; 0.5% catalyst; and 20% HAP,
when used.

Table XIV

EFFECT OF T-20 CONCENTRATION ON THE REACTION OF
2,4-DICHLOROPHENYL N-PHENYLCARBAMATE WITH n-AMYL
ALCOHOL IN BENZENE IN THE PRESENCE OF HAP AT 60°C

<u>T-20</u> <u>%</u>	<u>n-Amyl Alcohol</u> <u>% remaining after 1 hr</u>
0.5	91
3.0	80
20.0	71

^aReactants conc., 0.5M; 20% HAP.

The work to date with blocked isocyanates has led to the following conclusions.

a. While much remains to be learned (for example, what happens to the eliminated block in a propellant system?), the method has feasibility.

b. Since HAP has an inhibiting effect on the dissociation of carbamates, more active blocking agents (dissociation at lower temperature, below 40°C) are desirable.

c. combinations of easily dissociated carbamates and isocyanates may work better than the carbamates alone.

Table XVI

REACTION OF PHENYL ISOCYANATE BLOCKED WITH VARIOUS
COMPOUNDS WITH n-AMYL ALCOHOL AT 60°C IN BENZENE

Blocked Group	Catalyst	Oxidizer	Time, Hours	n-Amyl Alcohol % remaining
4-Chlorophenol	none	none	18	96
	none	HAP	18	97
	none	none	26h	95
	none	HAP	26h	95
	T-20	HAP	18	90
2,4-Dichlorophenol	none	none	68	34
	T-20	none	68	25
	none	HAP	68	90
	T-20	HAP	68	51
2,4,6-Trichlorophenol	none	none	68	72
	T-20	none	68	15
	none	HAP	68	97
	T-20	HAP	68	44
2-Chloro-4-Nitrophenol	none	none	68	33
	T-20	none	68	9
	none	HAP	68	97
	T-20	HAP	68	51
2,2,2-Trifluoroethanol	T-20	none	3	72
	T-20	HAP	3	81
	T-20	none	72	66
	T-20	HAP	72	76

4. Propellants

Propellants containing HAP as an oxidizer were prepared with various ratios of Carwinate 125M (a low melting solid diisocyanate) and E-246 at an 82% solids and 33% plasticizer level in order to obtain curing and castability data. All the mixes were dry and none cured after 4 days at 40°C. A batch with only E-246 as a curing agent did cure at this temperature but the castability was poor. The properties of the propellant were ρ_c , 20 psi; α_c , 30 psi; η_{sp} , 21%; η_v , 18%; E_c , 8 psi. Wetting agents such as lecithin and N,N-diphenylurea did not improve castability. Purified E-246 was used. When purified, the functionality of the E-246 may not be high enough. Untreated E-246 will be used.

E-246 blocked with 2,4-dichlorophenol as a curative gave a propellant with good castability but after 6 days at 60°C, had not cured.

As indicated by model compound studies the interference of HAF with the dissociation of the carbamate is the probable cause for the lack of cure in this propellant.

More studies are needed, especially with NH_4ClO_4 to establish a control for this type of curing system.

C. TASK FOUR

1. Introduction

Task Four involves the aging of propellants prepared under Tasks One and Two. It further includes the testing at 350°F for selected Task One propellants and the temperature cycling of propellants made with a GTI replacement.

2. Conventional Propellants

The aging of conventional propellants has been stopped because no further useful information was being generated. New propellants will be placed in aging as they are prepared.

3. Advanced Propellants

The advanced propellant samples have been stored at 80°F over Drierite (0% relative humidity) and at 30% relative humidity for up to 14 months, Table XVII.

Table XVII

AGING OF TELAGEN 8 PROPELLANTS CONTAINING ADVANCED FUELS

<u>Fuel</u>	<u>Storage time, months</u>	<u>Hardness, Shore A</u>		
		<u>Initial</u>	<u>Relative Humidity, %</u>	
			<u>0</u>	<u>30</u>
Me	14	74	75	76
LMH-2	14	68	75	70
LMH-1	8	48	59	57

The propellants exhibit little change in Shore A hardness. The LMH containing propellants show a slightly larger increase in hardness than the Me propellant.

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<p>The study of saturated prepolymers as propellant binder ingredients was centered predominantly on partially (50-60%) saturated prepolymers. The partially saturated propellants showed a threefold improvement of properties at -75°F. The type of crosslinker, OTI, OTHO, or LHT-240, did not affect the properties in a major fashion. The study of the LHT-240 which improved the low temperature properties of partially saturated propellants made on an I&AD program is continuing. Because more emphasis was being placed on partially saturated prepolymers, the oxidative surface hardening of binders made with saturated, partially saturated, and unsaturated prepolymers was investigated. The saturated binders showed no surface hardening after eight weeks at 80°C. Initially, the partially saturated binder hardened more rapidly than the unsaturated one, but the difference decreased with time. After eight weeks the unsaturated binder was hardening more rapidly. Propellant stability was greatly improved by a copper (II) additive and the feasibility of isocyanate-cured propellants for very high temperature use was demonstrated.</p> <p>The use of blocked isocyanates as cure agents for propellants with advanced oxidizers was studied in model systems. Carbamates which dissociate at 60°C to produce isocyanate were tested in the presence of oxidizers. Tin catalysts help and oxidizers inhibit the cure reaction. Carbamates with dissociation temperatures of 30° to 40°C are desirable.</p>		

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